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TITLE OF INVENTION

WIRING STRUCTURE AND ELECTRODE OF SEMICONDUCTOR DEVICE AND METHOD OF
MANUFACTURING THE SAME

APPLICANT(S) FOR DO/EO/US

Kimihiro MATSUSE, et al

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☐ A change of power of attorney and/or address letter.
18. ☐ Certificate of Mailing by Express Mail
19. ☒ Other items or information:

Notice of Priority

Drawings (4 sheets)

Two Articles 34, Amended Sheets 31-36

Request For Consideration of Documents Cited in International Search Report

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DESCRIPTION

WIRING STRUCTURE AND ELECTRODE OF
SEMICONDUCTOR DEVICE AND METHOD OF
MANUFACTURING THE SAME

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Technical Field

The present invention relates to a wiring
structure and an electrode of a semiconductor device,
and a method of manufacturing the same.

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Background Art

Generally, to manufacture a semiconductor
integrated device such as a semiconductor integrated
circuit, film-formation, oxidative diffusion, etching
and the like are repeatedly applied onto a semicon-
ductor wafer to form numeral transistors, capacitors,
and resistances, and thereafter these elements are
connected with a wiring pattern. Furthermore, since
the development of a high-performance integrated
circuit and a multi-functional integrated circuit has
been demanded, a further reduction of wiring width and
higher integration of the elements are demanded.
Moreover, a multi-layered structure has come to be
employed in which circuits themselves are stacked one
upon the other with an insulating layer interposed
between them.

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Since a sectional area of the wiring and
a connecting portion is reduced under these
circumstances, there is a tendency of increasing

resistance. It follows that, as a wiring material, copper tends to be used in place of aluminium used generally at present. This is because copper is highly resistant to electromigration and its resistivity is relatively low even though form-formation is not so easy as aluminum.

Usually, as a gate electrode used in a transistor element, a doped polysilicon layer is used alone or a double layered structure electrode is used which is formed by stacking a molybdenum silicide layer or a tungsten silicide layer on the doped polysilicon layer. However, to further reduce the resistivity, an attempt has been made to replace upper silicide layer of the double-layered gate electrode with a single metal layer, for example, a tungsten layer.

Incidentally, copper and tungsten themselves are highly active metals, so that they are likely to react with other elements. For example, metal copper has a large diffusion coefficient, so that it diffuses and segregates into Si, SiO₂ or the like, causing defects. As a result, not only resistance value increases but also exfoliation occurs.

When a metal tungsten film is used as one of the layers of the gate electrode of the double layered structure, the silicon atoms of the lower doped polysilicon layer and tungsten of the upper metal tungsten layer are mutually diffused and react with

each other to produce tungsten silicide having a large resistivity.

To prevent the reaction between the metal copper and the metal tungsten, it is possible to use a barrier metal such as TiN (titanium nitride) as conventionally used. However, the TiN layer is not a preferable barrier metal because affinity, in other words, adhesiveness, with the metal copper film and the metal tungsten film, is not satisfactory.

Recently, the semiconductor integrated circuit has been desired to be formed in more integrated and more multi-layered structure and operated at a higher speed. To satisfy these demands, it is required to reduce a resistivity of a gate electrode, for example, by reducing the thickness of individual layers and to increase an aspect ratio (a high aspect ratio) during etching processing.

However, if the thickness of a tungsten film constituting the gate electrode is reduced, the tungsten film degrades in adhesiveness to an underlying layer, for example, the polysilicon layer, and in heat resistance. It is also possible herein that a conventionally known TiN film is interposed between both layers as a barrier metal. However, in this case, the adhesiveness between the TiN film and the polysilicon film at the interface degrades, causing exfoliation.

Disclosure of Invention

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An object of the present invention is to provide a wiring structure and an electrode of a semiconductor device including a barrier metal which is effective for a metal copper film and a metal tungsten film, and to provide a method of manufacturing the same. Another object of the present invention is to provide a gate electrode excellent in characteristics even if the thickness is reduced and a method of manufacturing the same.

To attain the aforementioned object, the wiring structure of the semiconductor device according to the present invention comprises

15 a first conducting layer electrically connected to a semiconductor element or a wiring element formed on a semiconductor substrate;

a barrier metal formed on the first conducting layer; and

20 a second conducting layer formed on the barrier metal and electrically connected to the first conducting layer via the barrier metal;

in which the barrier metal is formed of WN_x (tungsten nitride) or WSi_xN_y (tungsten silicide nitride).

25 Furthermore, the present invention is directed to an electrode of a circuit element formed on a semiconductor substrate, comprising a polysilicon

(5)

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Furthermore, the present invention is directed to a method of forming a gate electrode of a transistor formed on a semiconductor substrate, comprising

forming a polysilicon layer on a gate oxide film
5 formed between a source and a drain of the transistor;

forming a barrier metal of WN_x (tungsten nitride) or WSi_xN_y (tungsten silicide nitride), thereby forming a metal layer on a barrier metal.

Brief Description of Drawings

10 FIG. 1 is an enlarged sectional view showing a barrier metal applied to Cu dual damashine wiring.

FIG. 2 is an enlarged sectional view showing a barrier metal applied to a contact hole.

15 FIG. 3 is an enlarged sectional view showing a barrier metal applied to a gate electrode.

FIG. 4 is an enlarged sectional view showing a barrier metal applied to a capacitor electrode.

FIG. 5 is a schematic structural view showing a processing apparatus for forming a barrier metal.

20 FIGS. 6A to 6F are views for use in explaining a Cu dual damashine process.

FIG. 7 is an enlarged view showing a part of the electrode shown in FIG. 3.

25 FIG. 8 is an enlarged sectional view of a gate electrode using Ta_2O_5 as a gate oxide film.

FIG. 9 is data for comparing the gate electrode according to the present invention to a conventional

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gate electrode.

Best Mode for Carrying Out the Invention

Now, embodiments of the present invention will be explained with reference to the drawings.

5 FIG. 1 is an enlarged sectional view showing a barrier metal applied to Cu dual damashine wiring. FIG. 2 is an enlarged sectional view showing a barrier metal applied to a contact hole. FIG. 3 is an enlarged sectional view showing a barrier metal applied to a gate electrode. FIG. 4 is an enlarged sectional view showing a barrier metal applied to a capacitor electrode.

10 The dual damashine process for forming Cu dual damashine wiring as shown in FIG. 1 is used for the multi-layered structure of wiring to attain a high-performance and multi-functional device in a semiconductor integrated device, namely, a semiconductor integrated circuit. More specifically, in the case where wiring is formed in the multi-layered structure, an upper layer wiring element is connected to a lower layer wiring element. At this time, this process makes it possible to form wiring and via-plug simultaneously, with the result that the number of steps, and the cost for wiring can be successfully reduced, and the aspect ratio can be successfully high.

25 In FIG. 1, reference numeral 2 is, for example, a substrate such as a semiconductor wafer, a reference

numeral 4 is a lower-layer wiring element (conducting layer) formed on a surface of the substrate 2. The lower-layer wiring element 4 is insulated by, for example, SiO_2 insulating film 6 formed therearound.

5 The lower-layer wiring 4 is formed of, for example, a metal copper thin film. Reference numeral 8 is an interlayer insulating film made of SiO_2 formed by SOG (Spin On Glass) so as to cover the SiO_2 insulating film 6 and the lower-layer wiring element 4. The interlayer
10 insulating film 8 is formed by coating in accordance with SOG as mentioned above, so that a relatively large number of oxygen molecules are contained.

Reference numeral 10 is a via-hole formed in the interlayer insulating film 8 so as to expose
15 a part of the lower-layer wiring element 4. Reference numeral 12 is a wiring groove formed in the surface of the interlayer insulating film 8. Reference numeral 14 is a thin barrier metal of WN_x (tungsten nitride; $x = 0.5-1$) or WSi_xN_y (tungsten silicide nitride; $x = 0.01-0.2$, $y = 0.02-0.2$) according to the present
20 invention. The barrier metal is formed on an inner wall surface of the via-hole 10 and on an inner wall surface of the wiring groove 12. Reference numeral 16 is an upper layer wiring element (conducting layer)
25 formed of, for example, a metal copper. When the wiring is formed, the via-hole 10 is filled with the metal copper, with the result that a via-hole plug 16A

is simultaneously formed.

In this case, the width L1 of the wiring element 16 is 1 μm or less, for example, about 0.2 μm . The thickness L2 of the barrier metal 14 is from about 0.005 to 0.05 μm .

As described in the above, in the dual damashine process, since the thin barrier metal 14 formed of WN_x or WSi_xN_y is interposed between the upper-layer wiring element 16 made of a copper thin film and the interlayer insulating film 8 formed by SOG, and between the via-hole plug 16A made of metal copper and the interlayer insulating film 8 formed by SOG, metal copper of the via-plug 16A and the upper-layer wiring element 16 cannot be diffused into the interlayer insulating film 8. It is therefore possible to prevent the occurrence of segregation and defects. Therefore, the resistance of the via-hole plug 16A and the upper-layer wiring element 16 can be maintained at a low value. In addition, since the adhesiveness does not degrade, it is possible to prevent the metal copper from peeling off.

In the modified example thus constituted, either one of the lower-layer wiring element 4 and the upper-layer wiring element 16 is formed of any one of Al, W, and Cu. The other one of the lower-layer wiring element 4 and the upper-layer wiring element 16 is formed of W or Cu.

FIG. 2 is a view showing the barrier metal of the present invention applied to a contact hole.

In the figure, reference numeral 18 is a source or a drain (conducting layer) of a transistor formed in the substrate 2. Explanation will be made by regarding reference numeral 18 as the source. Reference numeral 20 is an interlayer insulating film which covers the entire transistor including the source 18, thereby insulating it. The insulating film 20 is formed of a SiO_2 film formed by SOG in the same manner explained in FIG. 1. Reference numeral 22 is a contact hole to expose the surface of the source 18 therein. On the inner wall surface of the contact hole and the upper surface of the interlayer insulating film 20, a thin barrier metal 14 made of WN_x or WSi_xN_y according to the present invention is formed. The contact hole 22 is filled with a contact hole plug 24A made of metal copper, and simultaneously, metal copper is stacked on the upper portion. The metal copper is then subjected to pattern etching to thereby form a wiring element (conducting layer) 24.

Note that, in the figure, the barrier metal 14 on the interlayer insulating film 20 is pattern-etched.

In this case, since the thin barrier metal 14 made of WN_x or WSi_xN_y is interposed between the interlayer insulating film 20 made of SiO_2 and the contact hole plug 24A made of metal copper, and between

the interlayer insulating film 20 and the wiring element 24, it is possible to prevent the metal copper from diffusing into the interlayer insulating film 20. Therefore, it is possible to prevent the occurrence of segregation and defects of the metal copper constituting these elements. It is therefore possible not only to maintain a low resistivity but also to prevent the deterioration of adhesiveness, with the result that exfoliation can be prevented.

In the aforementioned structure, the drain or source 18 is formed of silicon (Si). The wiring 24 may be formed of Al or W.

FIG. 3 is a view of the barrier metal of the present invention applied to the gate electrode. In the figure, reference numerals 18, 19 are respectively a source and a drain of the transistor device formed in the surface of the substrate 2. A thin gate oxide film 26 is formed between these. A gate electrode 28 is formed on the gate oxide film 26. The gate electrode 28 is formed in a three layered structure by stacking, for example, a phosphorus-doped polysilicon layer 30, a thin barrier metal 14 of WN_x or WSi_xN_y , and a metal layer 32 of tungsten, in the order from the bottom.

In this case, since the barrier metal 14 of the present invention is interposed between the polysilicon layer 30 and the metal layer 32, it is possible to

prevent silicon atoms of the polysilicon layer 30 and metallic atoms of the metal layer 32 from diffusing each other. As a result, it is possible to not only prevent the metal layer 32 from being converted into a silicide but also prevent formation of pits (vacant holes) that the resistance of the metal layer 32 can be prevented from increasing and exfoliation of the metal layer 32 can be prevented.

In the aforementioned structure, the metal layer 32 may be formed of Cu. The gate oxide film 26 is formed of any one of SiO_2 , SiOF , Ta_2O_5 and CF_x ($x = 1-4$).

FIG. 4 shows a structure of a capacitor to which the barrier metal of the present invention is applied.

A diffusion layer 17 serving as one of the electrodes of the capacitor is formed in the surface of the substrate 2. On the diffusion layer 17, a thin insulating layer 26 is formed as a dielectric layer of the capacitor. On the thin insulating layer 26, a three layered structure of the polysilicon 30/barrier metal 14/metal layer (W) 32 is formed as the other electrode of the capacitor. The barrier metal 14 is formed of WN_x or WSi_xN_y . With this structure, the metal layer 32 is not converted into a silicide, so that an increase in resistivity is prevented. In addition, the exfoliation of the metal layer 32 can be prevented.

In this case, since the barrier metal 14 of the present invention is interposed between the polysilicon layer 30 and the metal layer 32, it is possible to prevent metal atoms of the metal layer 32 from diffusing into the polysilicon layer 30 by the presence of the barrier metal 14. As a result, it is possible to prevent the metal layer 32 from being converted into a metal silicide layer. It follows that the resistivity of the metal layer 32 is prevented from decreasing and exfoliation of the metal layer 32 is prevented.

In the aforementioned structure, the metal layer 32 may be formed of Cu or Al. The gate oxide film 26 may be formed of any one of SiO_2 , SiOF , Ta_2O_5 , and CF_x ($x = 1-4$).

Next, we will explain a method of forming the aforementioned wiring structure and electrode.

FIG. 5 is a view showing a schematic structure of a processing apparatus for forming the barrier metal. The processing apparatus will be first explained. As shown in the figure, the processing apparatus has a cylindrical shape processing vessel 34 made of aluminium. In the vessel 34, a mounting pedestal 36 is arranged for mounting the substrate 2 thereon. Within the mounting pedestal 36, a heater 38 is provided for heating the substrate 2 to a predetermined process temperature. Note that a heating lamp may be provided

in a lower portion of the processing vessel to heat the substrate 2 by the lamp.

The processing vessel 34 and the mounting pedestal 36 are individually grounded. The mounting pedestal 36 also serves as a lower electrode when a high frequency is used. At the bottom of the processing vessel 34, an exhaust port 40 is provided. To the exhaust port 40, a vacuum exhaust system is connected by way of a vacuum pump 42. To the side wall of the processing vessel 34, a loadlock chamber 44 is connected via a gate valve 41 for transferring the substrate 2 to/from the processing vessel 34.

At the upper portion of the processing vessel 34, a shower head portion 48 having numerous gas spray holes 50 is provided via an insulating material 46. To the shower head portion 48, a high frequency power source 56 of, for example, 13.56 MHz is connected by way of a switch 52 and a matching circuit 54. If a high frequency power is applied, if necessary, to the shower head portion 48 to use it as an upper electrode, plasma processing can be performed. The method for applying a plasma is not limited to this. The high frequency power may be applied to a lower electrode, and alternatively, applied to both upper and lower electrodes.

Furthermore, a plurality of gas sources are connected to the shower head portion 48 via an

open/shut valve 58 and a mass flow controller 60.

As a gas source, a WF_6 source 62, a MMH (monomethylhydrazine) source 64, a SiH_4 (silane) source 66, an NH_3 source 68, a N_2 source 70, an Ar source 72, a H_2 source 74, a ClF_3 source 75 are provided in accordance with different purposes and selectively used. Furthermore, in place of SiH_4 gas, disilane (Si_2H_4) or dichlorosilane (SiH_2Cl_2) may be used.

Then, a method of forming the wiring structure of the present invention using the device constituted as mentioned above will be explained more specifically.

The method of forming the wiring structure of the present invention includes a method of forming the barrier metal at a stretch in one step. Herein below, the method will be explained successively. In this text, a case where dual damashine wiring (refer to FIG. 1) is formed by the aforementioned Cu dual damashine process will be explained as an example. Note that in the case where the barrier metal is applied to a contact hole, the method of forming the barrier metal is completely the same although the steps before/after the step of forming the barrier metal differ.

(1) One-step formation of WSi_xN_y (plasma-less)

In the first place, a method of forming a WSi_xN_y barrier metal in one step will be explained. Using another apparatus different from the processing

apparatus shown in FIG. 5 and in accordance with a known method, a SiO_2 interlayer insulating film 8 is formed by SOG so as to cover the entire surface of the substrate 2 including a SiO_2 insulating layer 6 and a lower-layer wiring 4, as shown in FIG. 6 (A). Subsequently, a wiring groove 12 is formed by etching in the interlayer insulating film 8 along a wiring pattern in accordance with a known method (FIG. 6 (B)). Furthermore, a via-hole 10 is formed by etching at a predetermined portion of the wiring groove 12 to expose the lower-layer wiring 4 therein (FIG. 6 (C)).

After processing is applied to the substrate 2, the substrate 2 is loaded into a processing apparatus shown in FIG. 4 to initiate the formation of the barrier metal.

After the substrate 2 is placed on the mounting pedestal 36 of the processing vessel 34, the processing vessel 34 is sealed airtight. The substrate 2 is maintained under a predetermined processing pressure and simultaneously a predetermined processing gas is introduced from the shower head portion 48 while the processing vessel 34 is vacuum-evacuated and maintained at a predetermined processing pressure. Under these conditions, a process for forming the barrier metal is carried out. By supplying WF_6 gas, SiH_4 gas, and MMH gas separately as processing gases and employing plasma-less thermal CVD (Chemical Vapor Deposition),

the barrier metal 14 of the $W\text{Si}_x\text{N}_y$ film is formed at a stretch to a predetermined thickness in one step (FIG. 6(D)).

As the substrate 2, an 8-inch wafer is used herein. The processing gases, WF_6 gas, SiH_4 gas, and MMH gas are supplied at flow rates of about 2-20 sccm, 10-300 sccm, and 1-10 sccm, respectively. The processing temperature is about 300-450°C. The processing pressure is about 0.4-80 Torr. In the case where dichlorosilane is used in place of silane, the other gases are supplied at the same flow rates and the same processing pressure is employed but the processing temperature is about 550-650°C. Note that these numerical values mentioned about as well as the numerical values which will be described later are only examples, so that these numerical values may be appropriately changed in order to obtain the most suitable conditions.

If this method is employed, it is possible to form the barrier metal 14 in one step. As a result, the number of the steps can be reduced.

When the formation of the barrier metal 14 is completed in this method, for example, the substrate 2 is unloaded from the processing apparatus.

Subsequently, metal copper is deposited on the surface of the substrate 2 as a wiring metal and by CVD (chemical Vapour Deposition) simultaneously fill the

via-hole 10 and the wiring groove 12. In this manner, the via-hole 10 is filled with the via-hole plug 16A and the upper-layer wiring 16 is formed in the wiring groove 12 (FIG. 6 (E)).

5 Note that the CVD processing of the metal copper may be carried out in the same processing apparatus as used in forming the barrier metal.

10 Subsequently, the substrate having the metal copper deposited thereon is taken out from the processing apparatus and subjected to CMP (Chemical Mechanical Polishing) to polish and remove unnecessary metal copper of the upper surface. The wiring pattern of the upper layer is thus formed (FIG. 6 (F)). In this manner, the Cu dual damashine wiring is
15 completed.

 In this embodiment, MMH gas is used as a gas for use in mixing nitrogen atoms into the barrier metal 14. However, in place of this, NH_3 gas or N_2 gas may be used. If necessary, an inert gas such as Ar gas
20 may be used as a carrier gas. In place of SiH_4 gas, dichlorosilane, disilane or the like may be used.

(2) One-step formation of WN_x (plasma-less)

 Then, we will explain a method of forming WN_x barrier metal in one step. The same manner is employed
25 in the steps except the step shown in FIG. 6 (D), so that we will explain only the manner employed in the step shown in FIG. 6 (D). In this case, the barrier

metal 14 consisting of the WN_x film is formed at a stretch to a predetermined thickness in one step by supplying WF_6 gas and MMH gas as processing gases and in accordance with the plasma-less thermal CVD method.

5 In the case of an 8-inch wafer, the processing gas, WF_6 gas is supplied at a flow rate of about 5-80 sccm and MMH gas at a flow rate of about 1-20 sccm. The processing temperature is about 300-450°C and the processing pressure is about 0.5 to
10 80 Torr.

In this case, since only two types of processing gases are used, the structure of a gas supply system can be drastically simplified. Also in this case, needless to say, NH_3 gas or N_2 gas may be used in place
15 of MMH gas.

(3) Two-step formation of WSi_xN_y

Then, we will explain a method of forming a WSi_xN_y barrier metal in two steps. In this case, after the step shown in FIG. 6 (C) is completed, the WSi layer is
20 formed in the processing apparatus shown in FIG. 5. WF_6 gas and SiH_4 gas are used as the processing gases. The processing gases are supplied with or without using the carrier gas such as Ar gas to deposit the WSi film by plasma-less thermal CVD. The processing gas, WF_6
25 gas is supplied at a flow rate of about 2-80 sccm and SiH_4 gas is at about 5-40 sccm in the case of an 8-inch wafer. The processing temperature is about 300 to

450°C. The processing pressure is about 0.5 to 80 Torr. Needless to say, dichlorsilane, disilane, or the like may be used in place of SiH_4 .

When the formation of the WSi film is thus
5 completed, supply of WF_6 gas and SiH_4 gas is shut off and then, MMH gas is supplied to nitride the WSi film, with the result that the WSi_xN_y barrier metal 14 is formed. At this time, the flow rate of the MMH gas is about 1 to 20 sccm. The processing temperature is
10 about 300 to 450°C. The processing pressure is about 0.5 to 10 Torr. In this manner, the formation of the barrier metal 14 is completed. The nitriding is performed by using MMH gas herein because the processing can be made at a low temperature, so that
15 a side reaction product is relatively rarely generated. It is therefore favorable to solve a problem with particles.

In this case, NH_3 gas or N_2 gas may be used in place of the MMH gas. Furthermore, it is preferable
20 that the WF_6 gas be completely removed by purging N_2 gas into the processing vessel 34, between the film formation step and the nitriding step. In particular, when the NH_3 gas is used in place of the MMH gas in the nitriding step, if the WF_6 gas remains in the
25 processing vessel, a side product, which is difficult to remove, is formed by the reaction between ammonia and fluoride gas. It is therefore preferred to

completely remove the WF_6 gas before the nitriding process. When the NH_3 gas is used, the processing temperature is about 300 to 450°C.

In the case where N_2 gas is used in place of MMH gas, the switch 52 is turned on to apply a high frequency power between an upper electrode (shower head portion) 48 and a lower electrode (mounting table) 36. In this manner, a plasma is generated in the interior of the vessel to perform the nitriding process for the surface of WSi film. At this time, the supply amount of N_2 gas is about 50-300 sccm, the processing temperature is about 300 to 450°C, and the processing pressure is about 0.1 to 5 Torr (each of the conditions is for 8 inch wafer).

As described in the above, if two steps are carried out in the same processing apparatus, it is possible to cut down the time required for transferring of the wafer. As a result, the throughput can be improved. Needless to say, the film formation step and the nitriding step may be performed in discrete processing apparatuses.

(4) Two-step formation of WN_x

Then, we will explain a method of forming a WN_x barrier metal in two steps. In this case, after the step shown in FIG. 6(C) is completed, a W layer is first formed in the apparatus shown in FIG. 5. At this time, WF_6 gas and H_2 gas are used as the

processing gases to deposit the W film by the plasma-less thermal CVD. The flow rates of the processing gases, WF_6 gas and H_2 gas are about 5-100 sccm and about 100-1000 sccm. The processing temperature is about 300-450°C, the processing pressure is about 1 to 80 Torr.

When the formation of the W film is completed in this way, the supply of the WF_6 gas and the H_2 gas is shut off, and subsequently, MMH gas is supplied and thereby nitrides the W film to form the WN_x barrier metal 14.

The flow rate of the MMH gas at this time is about 1-10 sccm; the processing temperature is about 300-450°C, and the processing pressure is about 0.1 to 5 Torr, in the case of an 8-inch wafer. In this manner, the formation of the barrier metal 14 is completed. The nitriding is performed by using MMH gas herein because the processing can be made at a low temperature, so that a side reaction product is relatively rarely generated. It is therefore favorable to solve a problem with particles.

In this case, NH_3 gas or N_2 gas may be used in place of MMH gas as explained in the above (3). Furthermore, it is preferable that the WF_6 gas be completely removed by purging N_2 gas into the processing vessel 34, between the film formation step and the nitriding step. In particular, when NH_3 gas is

used in place of MMH gas in the nitriding step, if the
WF₆ gas remains in the processing vessel, a side
product, which is difficult to remove, is formed by
the reaction between ammonia and fluoride gas. It is
5 therefore preferred to completely remove the WF₆ gas
before the nitriding process. When NH₃ gas is used,
the processing temperature is about 300-450°C.

When N₂ gas is used in place of MMH gas, the
switch 52 is turned on to apply a high frequency power
10 between the upper electrode (shower head portion) 48
and the lower electrode (mounting table) 36. In this
manner, a plasma is generated in the interior of the
vessel to perform nitriding process for the surface of
WSi film. At this time, the supply amount of N₂ gas is
15 about 50-300 sccm, the processing temperature is about
300 to 450°C, and the processing pressure is about 0.1
to 5 Torr.

As described in the above, if two steps are
carried out in the same processing apparatus, it is
20 possible to cut down the time required for transferring
of the water. As a result, the throughput is improved.
Needless to say, the film formation step and the
nitriding step may be performed in discrete processing
apparatuses.

25 The barrier metal 14 formed by each of the
aforementioned methods was checked for characteristics.
As a result, it was confirmed that the barrier metal

has sufficiently high barrier properties to oxygen atoms or silicon atoms.

Next, the gate electrode of the present invention and the method of forming the gate electrode will be explained.

Now, the gate electrode 28, which has been explained with reference to FIG. 3, will be explained more specifically. FIG. 7 is a magnified view of a part of the gate electrode shown in FIG. 3.

We will explain the case in which tungsten nitride (WN_x) is used as the barrier metal 14 as an example. As explained in FIG. 3, a source 18 and a drain 19 are formed at both sides of the gate oxide film 26 over the substrate 2 such as a single crystalline silicon semiconductor wafer, as explained in FIG. 3. As the gate oxide film 26, a silicon oxide film (SiO_2) is used.

For example, a phosphorus-doped polysilicon layer 30 is formed in the different film formation apparatus as mentioned above and in accordance with a known method, and thereafter, the substrate W is loaded into the film formation apparatus as shown in FIG. 5.

The WN_x film may be formed either by a single step using the aforementioned plasma-less CVD or by two-steps.

When the WN_x film is formed in the single step, WF_6 gas and MMH gas are supplied as the processing

gases to form the barrier metal of the WN_x film on the polysilicon layer 30 at a predetermined thickness in accordance with the plasma-less thermal CVD.

The processing gas, WF_6 gas is supplied at a flow rate of about 5-80 sccm and MMH gas at a flow rate of about 1-20 sccm, in the case of an 8-inch wafer. The processing temperature is about 300-450°C and the processing pressure is about 0.5 to 80 Torr.

In this case, since the number of gas types is only two, the structure of the gas supply system can be drastically simplified. NH_3 gas or N_2 gas may be used in place of MMH gas.

In the case where the WN_x film is formed in two steps, the W layer is first formed. At this time, WF_6 gas and H_2 gas are used as the processing gases to deposit the W film by the plasma-less thermal CVD. As the processing gas, WF_6 gas is supplied at a flow rate of about 5-100 sccm and H_2 gas at a flow rate of about 100-1000 sccm in the case of an 8-inch wafer. The processing temperature is about 300-450°C and the processing pressure is about 1 to 80 Torr.

When the formation of the W film is thus completed, supply of WF_6 gas and H_2 gas is shut off. Subsequently, MMH gas is supplied to nitride the W film, to obtain the barrier metal 14 of WN_x . At this time, the flow rate of the MMH gas is about 1 to 10 sccm, the processing temperature is about 300

to 450°C, and the processing pressure is about 0.1 to 5 Torr. In this manner, the formation of the barrier metal 14 is completed. The nitriding is performed by using MMH gas herein because the processing can be made at a low temperature, so that a side reaction product is relatively rarely generated. It is therefore favorable to solve a problem with particles.

In this case, NH_3 gas or N_2 gas may be used in place of the MMH gas. Furthermore, it is preferable that the WF_6 gas be completely removed by purging N_2 gas into the processing vessel 34, between the film formation step and the nitriding step. In particular, when the NH_3 gas is used in place of the MMH gas in the nitriding step, if the WF_6 gas remains in the processing vessel, a side product, which is difficult to remove, is formed by the reaction between ammonia and fluoride gas. It is therefore preferred to completely remove the WF_6 gas before the nitriding process. When the NH_3 gas is used, the processing temperature is about 300 to 450°C.

After the WN_x barrier metal 14 is thus formed in the single step or the two steps, an upper tungsten layer 32 is formed in the same processing vessel 34. The film formation conditions for the tungsten layer 32 are the same as in the film formation step of the W film performed before the WN_x layer is formed in the two-step process previously mentioned. Using WF_6

gas and H₂ gas as the processing gases, the W film is deposited to a predetermined thickness in accordance with the plasma-less thermal CVD. At this time, a flow rate of the processing gas, WF₆ gas, is about 5-100 sccm and the H₂ gas about 100-1000 sccm. The processing temperature is about 300 to 450°C. The processing pressure is about 1 to 80 Torr. At this time, each of the layers is set such that a design rule for the memory corresponding to, for example, 1G bit capacity is used. More specifically, the gate oxide film 26 is about 20Å thick, the polysilicon layer 30 is about 500Å thick, the barrier metal 14 is 50Å thick and the metal layer (tungsten) layer 32 is 500Å thick.

The tungsten layer 32 is formed in this manner to thereby form the gate electrode 28. The barrier metal 14 and the tungsten layer 32 are made of the same metallic material, namely, tungsten, so that they are continuously formed in the same film formation apparatus. Therefore, the loading/unloading operation of the substrate is not required, with the result that the yield can be improved.

Since the WN_x layer is used as the barrier metal in the polysilicon metal gate electrode, it is possible to obtain resistance at an extremely low value. In addition, adhesiveness and heat resistance between both layers can be maintained high and high barrier properties are exhibited. In particular, even

if the barrier metal 14 is reduced in thickness up to about 50Å, the sufficient barrier properties as mentioned above can be obtained. It is therefore possible to attain a thin-film and multi-layered semiconductor integrated circuit.

The gate electrode of the present invention and a conventional gate electrode generally used were checked for characteristics. The results are shown in FIG. 9.

In FIG. 9, Comparative Examples 1 and 2 show a conventional gate electrode. More specifically, Comparative Example 1 is the gate electrode formed of the polysilicon layer and the tungsten silicide layer. Comparative Example 2 is the gate electrode formed of the polysilicon layer and titanium silicide layer.

As is apparent from FIG. 9, the gate electrode of the present invention is excellent in both resistance value and heat resistance which are critical characteristics as the gate electrode. Furthermore, it is demonstrated that the gate electrode of the present invention is satisfactory in chemical resistance, that is, corrosiveness to hydrogen fluoride (HF), and in etching properties during the film formation. Note that the low etching property during the film formation means that the film thickness is controlled well. Therefore, it is possible to form a thin-film gate electrode can be formed with a high accuracy.

In contrast, in Comparative Example 1, heat resistance is good but a critical factor, resistance value, is considerably large. For this reason, Comparative Example 1 is not preferable.

5 In Comparative Example 2, the resistance value is large and heat resistance is lower than the reference value of 850°C. For this reason, Comparative Example 2 is not preferable.

10 In the aforementioned embodiments, the case where SiO₂ is used as the gate oxide film 26 is explained as an example. However, the present invention is not limited to this. Tantalum oxide (Ta₂O₅) enabling a further reduction of the film thickness may be used as the gate oxide film 26.

15 FIG. 8 is a magnified sectional view of the gate electrode when Ta₂O₅ is used as the gate oxide film. In the case of the gate electrode shown in FIG. 8, a WN_x barrier metal 14 is directly formed on the Ta₂O₅ gate oxide film 26 in place of using the polysilicon layer. On the barrier metal 14, the tungsten layer 32
20 is further formed.

The barrier metal 14 and the tungsten layer 32 are formed continuously in the same film formation apparatus, as shown in the above. Also, in this case,
25 the WN_x barrier metal 14 not only exhibits efficient barrier properties but also contributes to further reducing the thickness of the gate electrode 28 since

the polysilicon layer is not used. The total thickness of the gate oxide film 26, barrier metal 14 and the tungsten layer 32 can be reduced up to, for example, about 1000Å. As a result, a design rule of the memory of 4G bit capacity can be applied thereto.

Now, WN_x and WSi_xN_y used in the embodiments of the present invention can be cleaned with a gas including ClF_3 gas in the same manner as in other major films. If cleaning is performed every time a film is formed on the appropriate number of wafers, it is possible to suppress generation of particles to obtain a high-quality film.

In the aforementioned embodiments, the case where tungsten is used as a high-melting point metallic material, is explained as an example. The present invention is not limited to this. For example, molybdenum (Mo) may be used. Furthermore, in the aforementioned embodiments, the case where a semiconductor wafer is used as the substrate is explained as an example. However, the present invention is not limited to this. Needless to say, an LCD substrate and a glass substrate may be used.

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Amended pages filed 8-19-99

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526 Rec'd PCT/PTO 05 MAY 2000

CLAIMS

1. (deleted)
2. (deleted)
3. (deleted)

ART 34 AMDT

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4. (deleted)

5. (deleted)

6. (deleted)

9. An electrode of a circuit element formed on a
5 semiconductor substrate, comprising:

a polysilicon layer;

a barrier metal formed on the polysilicon layer;

and

a metal layer formed on the barrier metal,

10 wherein the barrier metal is formed of WSi_xN_y
(tungsten silicide nitride).

ART 34 AMDT

10. The electrode according to claim 9, wherein the electrode is a gate electrode of a transistor; the polysilicon layer is formed on a gate insulating film formed between a source and a drain of the transistor.

5 11. The electrode according to claim 9 or 10, wherein the metal layer is formed of W or Cu.

12. The electrode according to claim 11, wherein the gate insulating film is formed of any one of SiO_2 , SiOF , Ta_2O_5 , and CF_x .

10 13. A gate electrode of a transistor formed on a semiconductor substrate, comprising:

a gate insulating film formed between a source and a drain of the transistor;

15 a barrier metal formed on the gate insulating film; and

a metal layer formed on the barrier metal, wherein the barrier metal is formed of WSi_xN_y (tungsten silicide nitride).

20 14. The electrode according to claim 9, wherein the electrode is a capacitor electrode and the polysilicon layer is formed on an insulating film.

15. The electrode according to claim 14, wherein the metal layer is formed of any one of Al, W, and Cu.

25 16. The electrode according to claim 15, wherein the insulating film is formed of any one of SiO_2 , SiOF , Ta_2O_5 , and CF_x .

17. (deleted)

ART 34 AMDT

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18. (deleted)

19. (deleted)

ART 34 AMDT

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20. (deleted)

23. (deleted)

24. A method of forming a gate electrode of
a transistor formed on a semiconductor substrate,
5 comprising

forming a barrier metal of WSi_xN_y (tungsten
silicide nitride) on a gate insulating film formed
between a source and a drain of a transistor; and
forming a conducting layer on the barrier metal.

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25. A method of forming a gate electrode of a transistor formed on a semiconductor substrate; comprising

5 forming a polysilicon layer on a gate insulating film formed between a source and a drain of a transistor;

forming a barrier metal of WSi_xNy (tungsten silicide nitride) on the polysilicon layer; and

forming a conducting layer on the barrier metal.

10 26. The method according to claim 24 or 25, wherein the conducting layer is formed of W or Cu.

27. The method according to claim 24 or 25, wherein the gate insulating film is formed any one of SiO_2 , $SiOF$, Ta_2O_5 , and CF_x .

A B S T R A C T

A wiring structure of a semiconductor device according to the present invention comprises a first conducting layer for electrically connecting with a semiconductor element or a wiring element formed on a semiconductor substrate, a barrier metal formed on the first conducting layer, and a second conducting layer formed on the barrier metal, for electrically connecting with the first conducting layer via the barrier metal, in which the barrier metal is formed of WN_x (tungsten nitride) or WSi_xN_y (tungsten silicide nitride).

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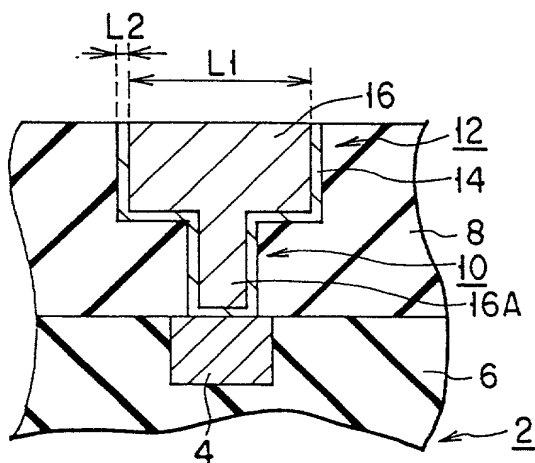


FIG. 1

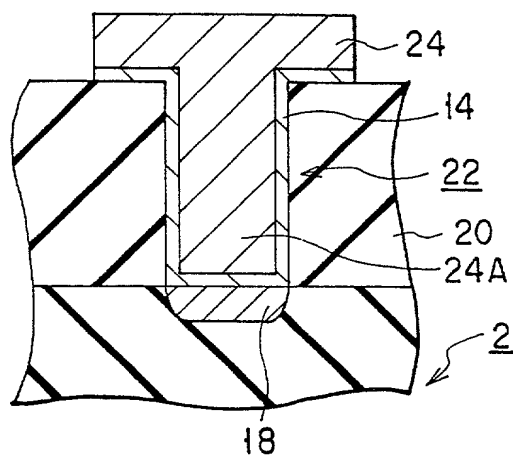


FIG. 2

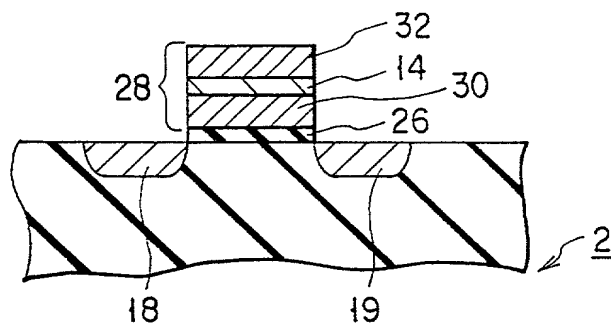


FIG. 3

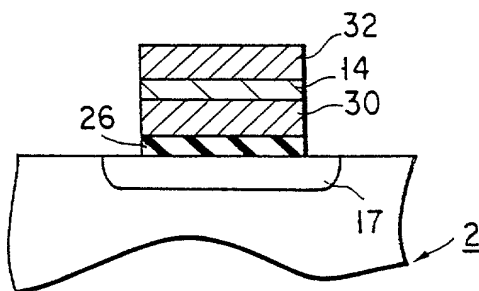
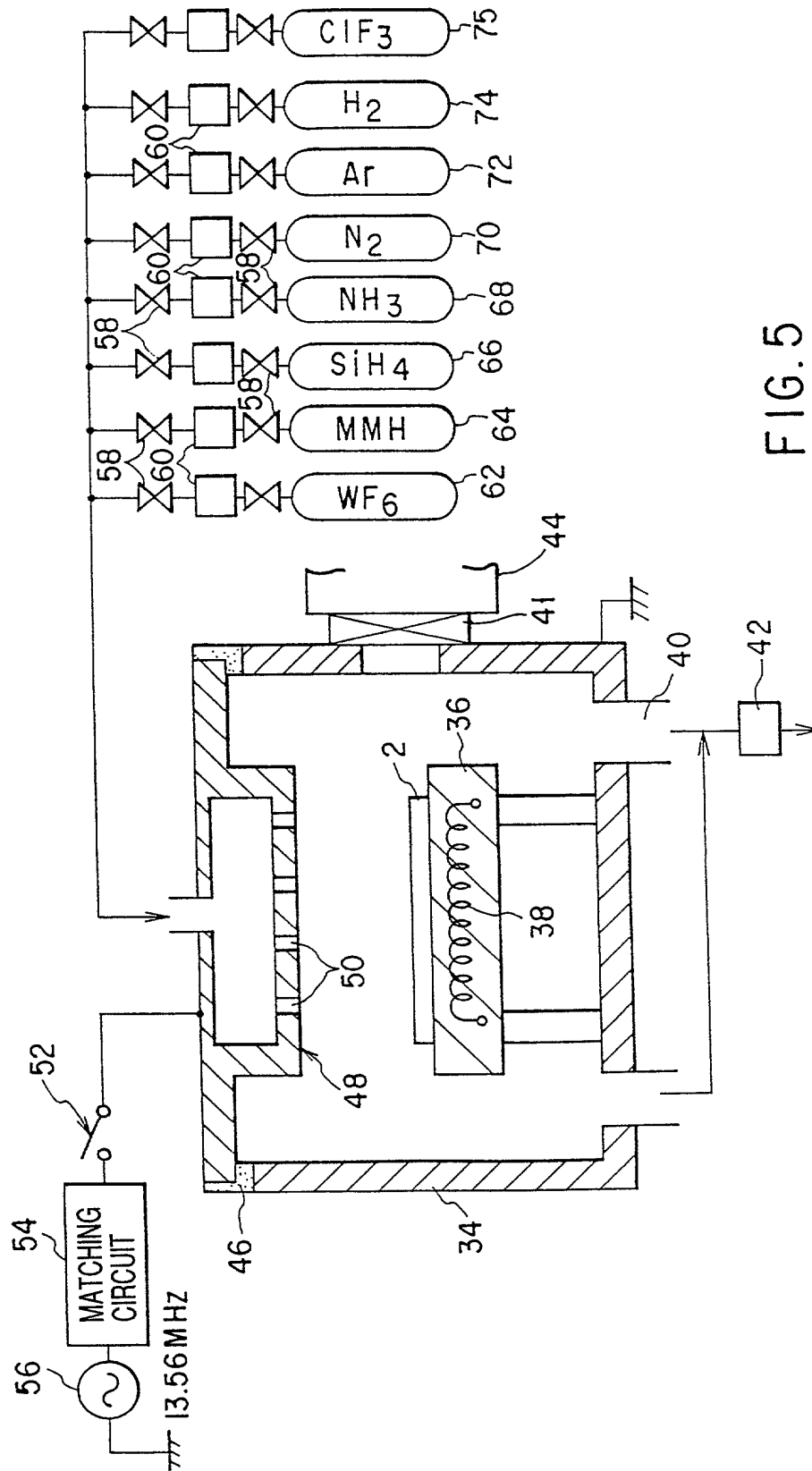


FIG. 4

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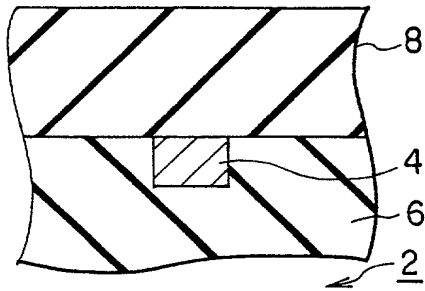


FIG. 6A

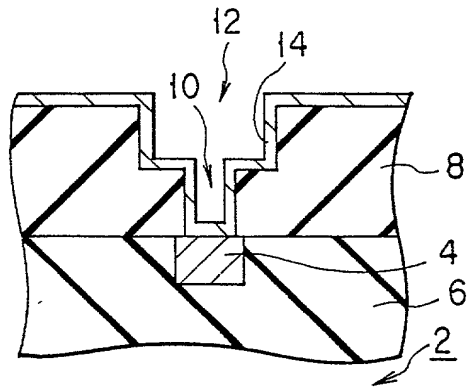


FIG. 6D

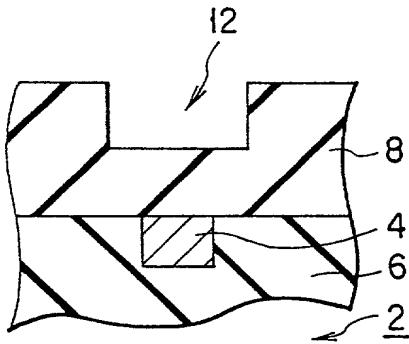


FIG. 6B

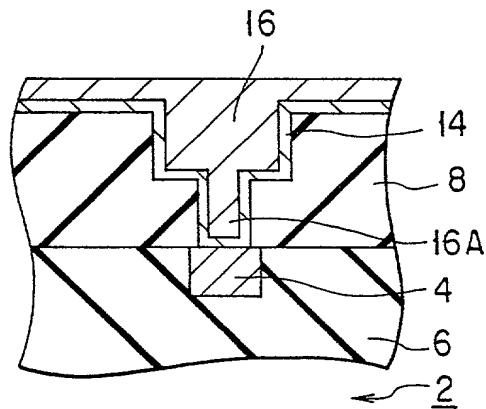


FIG. 6E

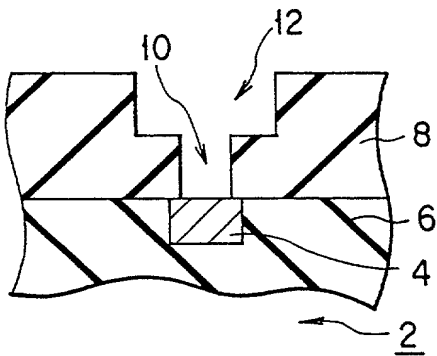


FIG. 6C

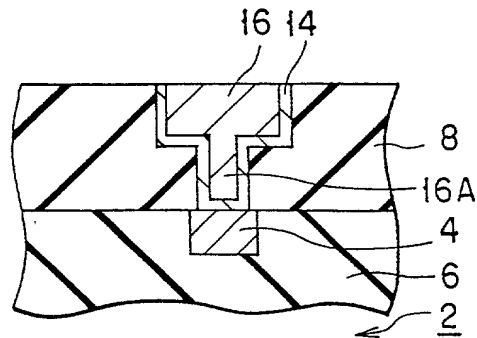


FIG. 6F

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FIG. 7

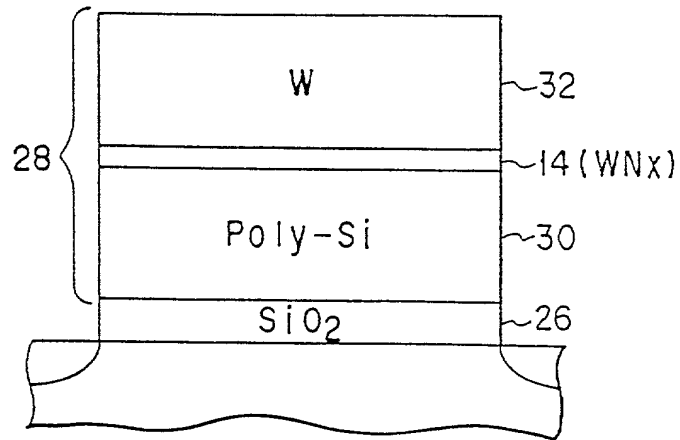
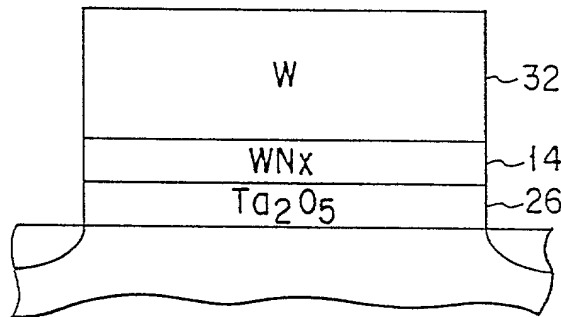


FIG. 8



	COMPARATIVE EXAMPLE 1	COMPARATIVE EXAMPLE 2	PRESENT INVENTION
STRUCTURE	Poly / WSi	Poly / TiSi	Poly / WN / W
RESISTANCE VALUE (uohmcm)	50 -60	20 -30	10
HEAT RESISTANCE (°C)	1000	800	900
CHEMICAL RESISTANCE (HF)	GOOD	POOR	GOOD
ETCHING AMOUNT DURING FILM FORMATION	LARGE	SMALL	SMALL

FIG. 9

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Declaration Power of Attorney For Patent Application

特許出願宣言書及び委任状 Japanese Language Declaration 日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

As a below named inventor, I hereby declare that:

私の住所、私書箱、国籍は下記の私の氏名の横に記載された通りです。

My residence, post office address and citizenship are as stated below next to my name,

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者であると（下記の名称が複数の場合）信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

半導体デバイスの配線構造、電極、及びこれらを形成する方法

WIRING STRUCTURE AND ELECTRODE OF SEMICONDUCTOR DEVICE AND METHOD OF MANUFACTURING THE SAME

上記発明の明細書（下記の欄で×印がついていない場合は、本書に添付）は、

The specification of which is attached hereto unless the following box is checked:

☐ 1998, 11月5日に提出され
米国出願番号または特許協定条約
国際出願番号をPCT/JP98/04983とし、
（該当する場合）1999, 4月8日 及び
1999, 8月19日に訂正されました。

☐ was filed on November 5, 1998
as United States application Number or
PCT international Application Number
PCT/JP98/04983 and was amended on
April 8, 1999 and August 19, 1999 (if applicable).

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第37編第1条56項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56

Japanese Language Declaration

(日本語宣言書)

私は、合衆国法典第35編第119条(a)-(d)項又は第365条(b)に基づき下記の、米国以外の国の少なくとも一カ国を指定している特許協力条約365(a)項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

I hereby claim foreign priority under Title 35, United States Code, Section 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT international application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT international application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)
外国での先行出願

Priority Not Claimed
優先権の主張なし

9-319059 (Number) (番号)	JAPAN (Country) (国名)	05/11/1997 (Day/Month/Year Filed) (出願年月日)	<input type="checkbox"/>
10-207198	JAPAN	07/07/1998	<input type="checkbox"/>
			<input type="checkbox"/>
			<input type="checkbox"/>
			<input type="checkbox"/>

私は、第35編米国法典119条(e)項に基いて下記の米国特許出願規定に記載された権利をここに主張いたします。

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below

(Application No.)
(出願番号)

(Filing Date)
(出願日)

(Application No.)
(出願番号)

(Filing Date)
(出願日)

私は、下記の米国法典第35編120条に基いて下記の米国特許出願に記載された権利、又は米国を指定している特許協力条約365条(c)に基づく権利をここに主張します。また、本出願の各請求範囲の内容が米国法典第35編112条第1項又は特許協力条約で規定された方法で先行する米国特許出願に開示されていない限り、その先行米国出願書提出日以降で本出願書の日本国内または特許協力条約国際提出日までの期間中に入手された、連邦規則法典第37編1条56項で定義された特許資格の有無に関する重要な情報について開示義務があることを認識しています。

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s) or 365(c) of any PCT international application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT Information application in the manner provided by the first paragraph of Title 35, United States Code, Section 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which become available between the filing date of the prior application and the national or PCT international filing date of application:

(Application No.)
(出願番号)

(Filing Date)
(出願日)

(Status: Patented, Pending, Abandoned)
(現況: 特許許可済、係属中、放棄済)

(Application No.)
(出願番号)

(Filing Date)
(出願日)

(Status: Patented, Pending, Abandoned)
(現況: 特許許可済、係属中、放棄済)

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Japanese Language Declaration

(日本語宣言書)

委任状: 私は、下記の発明者として、本出願に関する一切の手続きを米特許商標局に対して遂行する弁理士または代理人として、下記の者を指名いたします。
(弁理士、または代理人の氏名及び登録番号を明記のこと)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (list name and registration number)

Norman F. Oblon (Reg. No. 24,618), Marvin J. Spivak (Reg. No. 24,913),
C. Irvin McClelland (Reg. No. 21,124), Gregory J. Maier (Reg. No. 25,599),
Arthur I. Neustadt (Reg. No. 24,854), Richard D. Kelly (Reg. No. 27,757),
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Robert T. Pous (Reg. No. 29,099), Charles L. Gholz (Reg. No. 26,395),
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Martin M. Zoltick (Reg. No. 35,745), Robert W. Hahl (Reg. No. 33,893),
Richard L. Treanor (Reg. No. 36,379), Steven P. Weihrouch (Reg. No. 32,829),
John T. Goolkasian (Reg. No. 26,142), Marc R. Labgold (Reg. No. 34,651),
Richard L. Chinn (Reg. No. 34,305), Steven E. Lipman (Reg. No. 30,011),
Carl E. Schlier (Reg. No. 34,426), James J. Kulbaski (Reg. No. 34,648),
Catherine B. Richardson (Reg. No. 39,007), Richard A. Neifeld (Reg. No. 35,299),
J. Derek Mason (Reg. No. 35,270) and Surinder Sachar (Reg. No. 34,423).

書類送付先:

Send Correspondence to
OBLON, SPIVAK, MCCLELLAND,
MAIER & NEUSTADT, P.C.,

Fourth Floor,
1755 Jefferson Davis Highway,
Arlington, Virginia 22202

直通電話連絡先:

Direct Telephone Calls to: (name and telephone number)
Telephone No. (703) 413-3000
Facsimile No. (703) 413-2220

唯一のまたは第一発明者の氏名 松瀬 公裕	Full name of sole or first inventor Kimihiro Matsuse
同発明者の署名 日付	Inventor's signature Date Kimihiro Matsuse April 12, 2000
住所 日本国稲城市	Residence Inagi-shi Japan JPK
国籍 日本	Citizenship JAPAN
郵便の宛先 〒107-8481 日本国東京都港区赤坂5丁目3番6号	Post Office Address c/o Intellectual Property Dept., TOKYO ELECTRON LIMITED
東京エレクトロン株式会社 知的財産部内	3-6 Akasaka 5-chome, Minato-ku, Tokyo 107-8481 Japan

(第二以降の共同発明者に対しても同様に記載し、署名を
すること。)

(Supply similar information and signature for second
and subsequent joint inventors.)

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Japanese Language Declaration

(日本語宣言書)

第 2 共同発明者の氏名 (該当する場合)	Full name of 2nd joint inventor, if any
大槻 林 200	Hayashi Otsuki
同第 2 発明者の署名 日付	2nd Inventor's signature Date
	Hayashi Otsuki April 12, 2000
住 所	Residence
日本国中巨摩郡	Nakakoma-gun, Japan JPK
国 籍	Citizenship
日本	JAPAN
郵便の宛先 〒107-8481 日本国東京都港区赤坂5丁目3番6号	Post Office Address c/o Intellectual Property Dept., TOKYO ELECTRON LIMITED
東京エレクトロン株式会社 知的財産部内	3-6 Akasaka 5-chome, Minato-ku, Tokyo 107-8481 Japan
第 共同発明者の氏名 (該当する場合)	Full name of joint inventor, if any
同第 発明者の署名 日付	Inventor's signature Date
住 所	Residence
国 籍	Citizenship
郵便の宛先	Post Office Address
第 共同発明者の氏名 (該当する場合)	Full name of joint inventor, if any
同第 発明者の署名 日付	Inventor's signature Date
住 所	Residence
国 籍	Citizenship
郵便の宛先	Post Office Address

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